



## Research papers

## Increased organic contaminant residence times in the urban riverbed due to the presence of highly sorbing sediments of the Anthropocene

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## ABSTRACT

This study evaluates the hypothesis that increased organic-contaminant sorption and hence residence time in urban riverbed deposits may occur due to the presence of highly sorbing sediment components of anthropogenic origin that contain thermally altered carbonaceous materials (TACM). The hypothesis was confirmed through laboratory-batch studies examining tetrachloroethene (PCE) sorption on riverbed sediment samples from the highly urbanised River Tame headwaters catchment (Birmingham, UK) and the River Tern (Shropshire) providing a nearby rural benchmark. Urban-riverbed sorption was elevated with observed organic-carbon partition coefficient ( $K_{oc}$ ) values over an order of magnitude greater than rural values. The latter compare to the widely used US EPA geometric-mean  $K_{oc}$  and attributed to absorption-dominated partitioning into (recent) natural organic matter. Use of that mean is inappropriate for the urban riverbed, potentially underestimating retardation by an order of magnitude. Organic petrography confirmed the urban riverbed contained a high proportion of TACM-rich organic-matter particles to which significant adsorption might be expected; furthermore, elevated urban  $K_{oc}$  values were consistent with TACM-rich sediment literature estimates. The TACM source appears to be riverine transport of particulate matter from historical industrial/urban or coal-mining/processing activities prevalent upstream since the Industrial Revolution. Consequences of the increased urban riverbed residence time on attenuation and bioavailability assumption sensitivities were modelled. Under the standard assumption of sorbed contaminant being non-bioavailable, rapid rates of aqueous-phase biodegradation are necessary for complete attenuation within a riverbed. Conversely, if adsorbed contaminant is bioavailable, then complete attenuation is probable where highly adsorbing (Anthropocene urban) riverbed sediments are present, even for long half-lives. Therefore, Anthropocene-sediment occurrence may significantly influence modern-day contaminant fate within the urban riverbed; the principal implication being greatly increased sorption and residence times may occur in urban riverbeds than conventionally assumed. Further research should focus upon whether adsorbed contaminants have any bioavailability causing increased contaminant flux attenuation and surface-water quality protection.

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## 1. Introduction

The residence time of groundwater organic contaminants in riverbed sediments prior to discharge to surface-waters may be perceived as short compared with the time that the plume has spent in the aquifer prior. Riverbed sediments may, however, be rich in organic matter to which sorption of hydrophobic organic contam-

inants occurs leading to retarded contaminant transport, extended riverbed-residence times and delayed breakthrough. If riverbed conditions favour bio(geochemical) degradation of contaminants, then the combination of sorption and degradation may lead to an enhanced natural attenuation (NA) of contaminants and reduced, delayed or even completely attenuated contaminant discharge to a surface-water receptor. Assessment of riverbed reactivity and its influence upon contaminant residence time and fate at the groundwater – surface water interface (Krause et al., 2017) represents a key research focal point within the greater subsurface hydrological system residence (de Dreuz and Ginn, 2016).

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Our study focuses upon chlorinated aliphatic hydrocarbons (CAHs) that include the notorious groundwater contaminants trichloroethene (TCE) and tetrachloroethene (PCE). Prominence of these solvents not only relates to their ubiquitous historical use for degreasing, but also their dense non-aqueous phase liquid (DNAPL) properties resulting in deep aquifer penetration and subsurface persistence (Rivett et al., 2014; Yang et al., 2018). This persistence, coupled with often limited NA, may result in continuous discharge of plumes to surface waters (Ellis and Rivett, 2007; McGuire et al., 2004; Rønde et al., 2017; Weatherill et al., 2014). Site studies on these discharging plumes, and associated laboratory studies, have often focused upon biodegradation, the key mass-loss attenuation process (Atashgahi, et al., 2017; Freitas et al., 2015; Lee and Lee, 2015; Weatherill et al., 2018). We, however, contend that sorption of discharging CAH plumes in urban riverbeds demands closer scrutiny. Urban anthropogenic influences over decades or even centuries of the Anthropocene will have led to modification of the riverbed deposits, potentially causing them to have different sorption properties from those present under pre-urban conditions.

Sorption predominantly occurs to organic matter (OM) within the riverbed sediments. This material may be comprised of natural organic matter (NOM) as well as anthropogenic organic matter (AOM) arising from anthropogenic activities (Allen-King et al., 2002; Cornelissen and Gustafsson, 2004; Cornelissen et al., 2005; Grathwohl, 1990; Jeong et al., 2008; Kleinedam et al., 1999; Smith and Lerner, 2008). NOM within a riverbed setting may include gelified or non-gelified woody phytoclast (tissues and structureless humic/fulvic detritus), peat, seed coatings, bark, root, pollen, spores, lignin and fungal material. Whilst such materials may exist in ancient sediments, within riverbed settings, NOM is typically of recent origin due to its labile nature. Definition of AOM is more contentious. It includes OM whose nature has changed due to anthropogenic activity, notably heating to produce thermally altered carbonaceous material (TACM) (Allen-King et al., 2002; Jeong et al., 2008). It is also taken herein to include OM that occurs in the riverbed as a consequence of anthropogenic influence, typically urban – industrial historical activity. Coal particles arising from mining activity exemplify the latter. AOM may thus include hard coals, coke (mostly formed from coal carbonisation), soot from traffic or oil combustion, char mostly from coal combustion, residues from coal carbonisation, and coal- and petroleum-derived fluorescent materials (tar, oils and lubricants), organic-contaminated sediments and globules of (dense) non-aqueous phase liquids (NAPLs) (Grathwohl, 1990; Cornelissen et al., 2005). Sources include poorly controlled industrial effluent, mining and sewage discharges, urban runoff, illegal dumping and contaminated baseflows.

Sorption includes both partitioning (absorption) and adsorption of organic contaminants on the various forms of OM in the sediment (Allen-King et al., 2002; Wang et al., 2013). The absorption domain consists of amorphous organic matter such as humic and fulvic substances and lignin. The absorption process is conceptualised as contaminant hydrophobic phase-partitioning into the OM phase and is characterised by linear isotherms (Karickhoff et al., 1979). In contrast, adsorption occurs to more condensed organic matter with, in particular, TACM exhibiting very strong, non-linear adsorption (Allen-King et al., 2002; Cornelissen and Gustafsson, 2004). Allen-King et al. (2002) define TACM to encompass non-carbonate, carbon-containing matter that includes carbonaceous matter (CM) forms created by combustion and pyrolysis processes, such as soot and char, as well as by geological processes (diagenesis and catagenesis), such as coal and kerogen (Allen-King et al., 2002; Wang et al., 2013). TACM is particularly hydrophobic and rich in adsorption sites due to its very high surface area, (micro)porosity, greater aromaticity and lower O/C and

H/C ratios compared to non thermally-altered parent material (Allen-King et al., 2002; Cornelissen et al., 2005; Wang et al., 2013).

Critically, TACM is prevalent within the AOM category, but often (near) absent from recent NOM; recognising the exception of TACM arising from the erosion of near surface coal seams (Karapanagioti et al., 2000), TACM that may occur naturally in some near surface sediments or sedimentary rocks (e.g. Kleinedam et al., 1999), or deposition of fire-related particulates. Thus, the AOM-rich urban riverbed is expected to be TACM-rich and increased contaminant sorption and therefore residence times occur compared to pre-urban conditions. The potential significance of this, but not specifically within riverbed settings, is underlined by Wang et al. (2013) who collate PCE sorption literature that indicates much higher  $K_{oc}$  (organic-carbon partition coefficient) values may be justified in NA assessment when TACM is present and contaminant concentrations are low, i.e. in the case of the conceptual model we are proposing. Wang et al. (2013) and others (Allen-King et al., 2002; Arp et al., 2009) confirm TACM-influenced  $K_{oc}$  values may be 2 to 3 orders of magnitude greater than the empirically determined, very widely used, US EPA (1996) geometric mean  $K_{oc}$  of 265 l/kg, a value that better characterises the much lower absorption interaction (Wang et al., 2013).

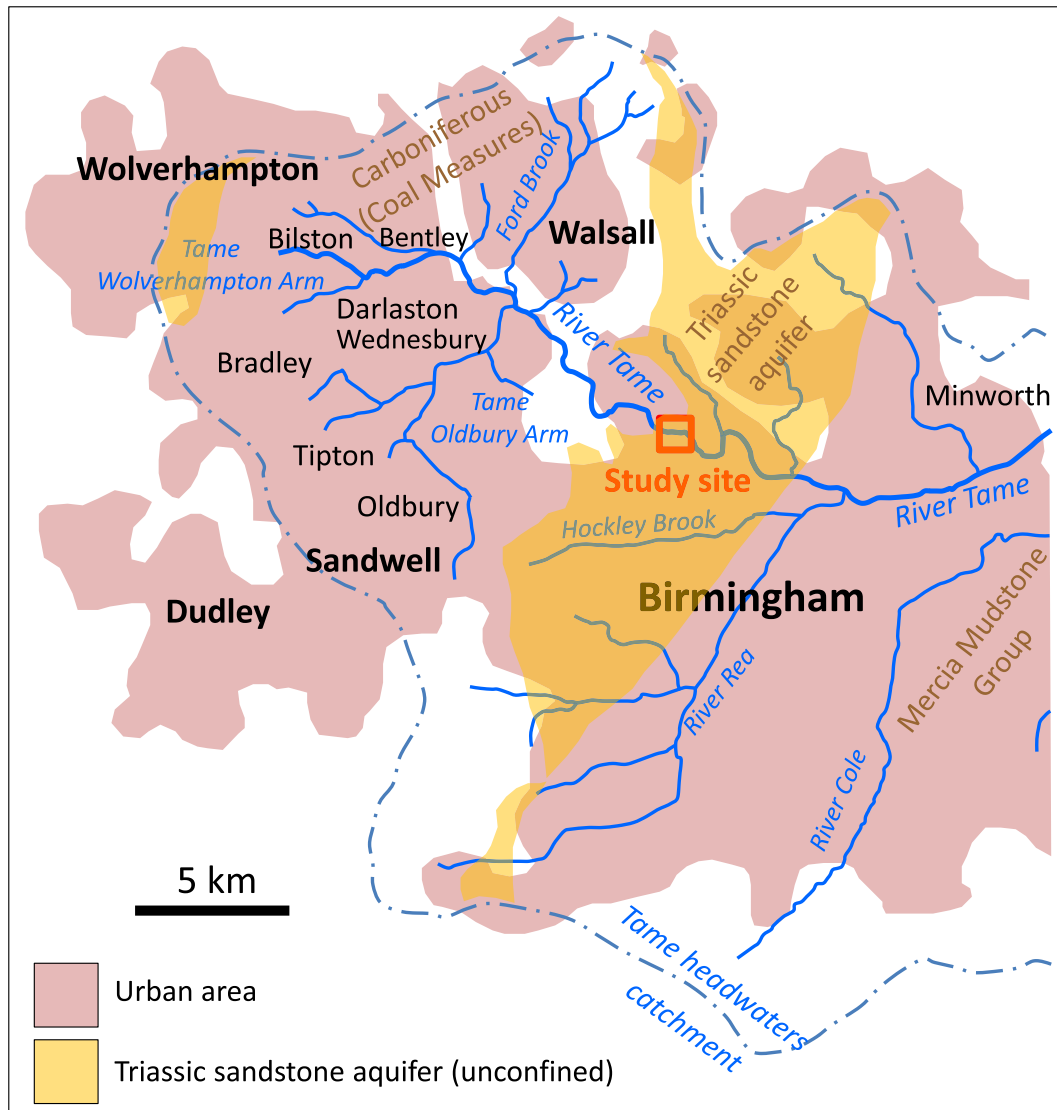
A further consequence of increased sorption is that assumptions on contaminant bioavailability become more critical (Cornelissen et al., 2005; Semple et al., 2003). Contaminants are typically modelled as bioavailable and able to biodegrade when present in the dissolved-phase but not when in the sorbed phase. Hence although increased sorption causes increased riverbed residence time, time spent within the dissolved phase remains unaltered resulting in no increase in time opportunity for biodegradation. Some bioavailability of sorbed contaminant could, however, lead to much increased timeframes for biodegradation. We consider the sensitivity of bioavailability assumptions in the urban riverbed setting.

We aim to evaluate our hypothesis that increased organic contaminant sorption and therefore residence time occurs in urban riverbed deposits due to the presence of highly sorbing sediment components of anthropogenic origin. The influence of the Anthropocene is hence proposed significant (Price et al., 2011). Our approach involves laboratory batch-sorption experiments and sediment organic-matter characterisation from a well-studied CAH groundwater plume discharge zone (Freitas et al., 2015). The study site is located in Birmingham, the UK's second largest city and one that has a significant industrial heritage. The site lies in the headwaters of the River Tame, arguably the UK's most urbanised catchment (Lawler et al., 2006). Similar data were obtained from the River Tern, which lies about 60 km to the northwest of Birmingham, in order to provide a rural benchmark against which to compare the urban system data. A semi-analytical model of riverbed solute transport is then used to explore the implications of the findings.

## 2. Study sites

### 2.1. Urban site setting

The study reach is located in north-west Birmingham on the River Tame headwaters, the catchment covering much of the greater West Midlands conurbation (Fig. 1). It is near the western boundary of the Triassic Sandstone aquifer that underlies Birmingham and the upper Carboniferous deltaic ('Coal Measures') sequence that underlies much of the highly urbanised 'Black Country' region to the west. The Tame arises in the urban Carboniferous and flows eastwards across Birmingham. The Coal Measures comprise a complex, heavily faulted, discontinuous geology with thin (c. 1 m) discrete coal bands (often mined out) set within a much



**Fig. 1.** Study site location within the Tame headwaters catchment. The solid geology (Powell et al., 2000) is simplified to show the Birmingham unconfined Triassic sandstone aquifer occurrence, with confining Mercia Mudstone Group present to the east and Carboniferous (Coal Measures) units to the west within the catchment. The urbanisation shown is based upon Lawler et al. (2006).

greater rock mass of layered fractured sandstones, siltstones, mudstones, and conglomerate. Overlying superficial deposits comprise alluvium with sands and gravels, mostly around the river and tributary channels, with a wider more extensive coverage of low permeability till in the upper tributary area except in the west around Bradley and Tipton (Fig. 1). Mean flow of the Tame at the study site is c. 200 Ml/d with a catchment area upstream of c. 220 km<sup>2</sup>. It is a relatively high-energy, 'flashy' river, frequently engineered to drain the West Midlands more efficiently.

#### 2.1.1. Urban influence upon riverbed sediments

The study area has been subject to significant urban influence with the Industrial Revolution foundational to the diverse industrial-urban landscape that emerged over the 18th to 20th centuries (Thomas and Tellam, 2006). Birmingham was internationally renowned as a centre of metals and engineering manufacturing underpinned by coal, limestone, iron-ore extraction and smelting in the Black Country. Coal mining in the Bilston – Darlaston area upstream, present since the 14th century, rapidly expanded in the 17th–18th centuries before declining in the 19th century, with over 130 mines closing during 1860 to 1928 in Bil-

ston alone (Lawler et al., 2006). Coal exploitation left not only a significant abandoned-mines legacy, but considerable contaminated land from smelting, coal carbonisation, coking, gasworks and heavy-industry activity (Parker, 2015). Heavy-industry decline to a more service-based economy has occurred since the 1960s with significant land remediation activity and re-development following.

Surface-water quality has been impacted by this heritage (Ellis and Rivett, 2007; Harkness, 1982; Severn Trent Water, 1976; Thoms, 1987). Rive Tame issues date back to at least the 1858 'sewage pollution nuisance case', with sewage treatment not becoming remotely adequate until several decades later (Rosenthal, 2007). Around 80% of the Tame dry-weather flow in the late 20th century was attributed to effluent discharge (NRA, 1996). Whilst industrial effluent pipe discharges to the Tame have declined, it was not until the 1970s that stringent regulation transpired. Elevated Ni, Cu, Cr and Zn remained obvious in the West Midlands within the 1986–96 survey of the greater Trent – Humber catchment (Harkness, 1982; Oguchi et al., 2000). Tame quality was categorised in the worst classes E/F (poor/bad) in 1999, but improving by 2006 to GQA (General Quality Assessment) Chemistry E and Biology D

(Rivett et al., 2011). Noting the river's entrainable riverbed sediment supplies being low compared to other UK rivers, Lawler et al. (2006) point to other sources of sediment – distal road or roof runoff, road gully pots, combined sewer overflows, former mine-workings and dislodged biofilms (from sewers). The Tame valley has long served as national road, rail and canal network hubs; highway runoff potentially accounting for 50% of suspended solids in urban catchments (Ellis, 1999). Severn Trent Water (1976) indicate tributaries around Darlaston (Fig. 1) received turbid water ascribed to particulates within shallow (<120 m deep) abandoned coal-mine discharges. Anthropogenic contamination of riverbed sediments in the study reach is inevitable.

Regarding groundwater-plume discharges, widespread and persistent contamination of the Birmingham aquifer by CAHs has been observed since the 1980s, but may stem from releases dating back to the 1930s (Rivett et al., 2012). Our 50-m long study reach forms the most upstream reach on the Tame observed to be contaminated by CAH groundwater plume discharges in the survey by Ellis and Rivett (2007) of the 7 km of river reach crossing the Birmingham unconfined sandstone (Fig. 1). Work at the site has largely focused upon the spatially variable biodegradation of the TCE plume occurring within the riverbed (Freitas et al., 2015).

## 2.2. Rural comparison site

A rural site on the River Tern, Shropshire was selected to provide benchmark comparison with the urban site. The Tern, located 60 km north-west of Birmingham, is a predominantly agricultural catchment of about 880 km<sup>2</sup> (Adams et al., 2003). It has many similarities to the Tame, being a small lowland river in an area of gently rolling topography, underlain by and in receipt of baseflow from the (East Shropshire) Permo-Triassic Sandstone with a variable covering of Quaternary tills, sands, and alluvium, and an annual rainfall of around 700 mm (Cuthbert et al., 2010). The sampling site is at Helshaw Grange where the river is about 6 m wide with generally steep vegetated banks, and is underlain by alluvium and Quaternary deposits (Weatherill et al., 2014). Riverbed deposits are predominantly fine to medium-grained sands with very little gravel, but some woody debris. Flow is about 70 Ml/d from a catchment of about 93 km<sup>2</sup>, equivalent to about a third of the flow of the Tame site.

## 3. Methods

### 3.1. Tame (urban catchment) riverbed sampling

The multilevel sampler network and other study reach infrastructure and sampling methods are detailed by Freitas et al. (2015) and Rivett et al. (2008); we describe only the riverbed sediment sampling relevant to the present study. Retrieval of riverbed samples was challenging due to the well-armoured, firm, and densely-packed riverbed nature and frequency of large pebbles and cobbles (Freitas et al., 2015). Riverbed sediment samples for  $f_{oc}$  (fraction of organic carbon content) and  $K_d$  (sorption (soil-water) partition coefficient) determination and for organic matter characterisation in the laboratory were obtained by manual coring and grab sampling.

Cores were obtained using a stainless steel tube (4.6 cm diameter) containing a PVC-liner tube. This was driven into the riverbed using a sledgehammer; a rubber bung was inserted into the top of the steel tube and the tubes withdrawn together. The plastic tube insert was then removed, cut to size and tube ends sealed with wax. The success rate of coring was poor. Although five successful cores were obtained, these involved careful selection of locations in areas of softer, partially consolidated sediment with few cobbles.

As such, representation of the entirety of sediment types in the Tame was not achieved, though later freeze coring, reported in Freitas et al. (2015), did provide increased opportunity for inspection of in-situ sediment heterogeneity (and is exemplified later herein).

A total of 16 grab samples were taken from the River Tame for batch-sorption experiments during sediment characterisation and mapping of the riverbed deposits. Grab samples were obtained of a representative selection of hummock and armoured bedforms. Also, supporting grab samples were obtained with depth in the vicinity of the core sites. Grab samples were excavated by spade from discrete depth intervals and bagged in containers as rapidly as possible to minimise loss in the flowing water column.

### 3.2. Tern (rural catchment) riverbed sampling

Seven riverbed cores, two of which were used in the current study for  $K_d$  determination, were obtained from the River Tern. Cores were taken from a reach close to that detailed by Weatherill et al. (2014) and characterised by low flow, woody debris materials settled on soft, predominantly sandy sediments. An Eijkkelkamp Beeker sampler for soft sediments was used to extract cores of sediment where possible. For firmer sediments, 1 m lengths of plastic tubing (5 cm diameter) were driven into the sediment using a fence-post driver and core withdrawn under suction by use of a rubber bung inserted at the tubing top; around 90% recovery was achieved.

### 3.3. Laboratory methods

#### 3.3.1. $f_{oc}$ (fraction of organic carbon content) measurement

The  $f_{oc}$  of sediment samples was measured using the Solid Sample Module of a Shimadzu Total Organic Carbon Analyser (SSM-5000A). Infrared is used to measure CO<sub>2</sub> given off during sample combustion to determine sample carbon. The Solid Sample Module contains one furnace at 900 °C to combust all carbon (organic and inorganic) and a second at 200 °C to combust sample pre-treated with phosphoric acid and determine the inorganic carbon fraction. The organic carbon is determined by difference. Prior to analysis, the sediments were oven-dried for 24 h at 105 °C and pulverized using a TEEMA mill until they passed through a 250 µm sieve. Separate calibrations were performed for total and inorganic carbon (TC and IC) using, respectively, glucose (40% C) over a range of 0.8 to 30 mg C, and sodium carbonate (11.3% C) over a range of 0.4 to 20 mg C. Samples of c. 0.1 g were weighed into combustion boats and analysis done in triplicate for both total carbon and inorganic carbon.

#### 3.3.2. Batch sorption experiments

PCE was used for batch sorption studies in preference to TCE due to its greater hydrophobicity allowing easier measurement, and due to the larger literature base (e.g. Allen-King et al., 1995, 1998; Ball and Roberts, 1991; Rivett and Allen-King, 2003). Sediment samples were oven dried at 105 °C for 24 h and pulverised using a mortar and pestle until fine enough to pass a 250 µm sieve. This reduces the time to reach equilibrium without influencing overall sorption magnitude (Ball and Roberts, 1991). Sediments were then homogenised using a riffle splitter and divided for use in the batch experiments. A series of 40 ml glass vials with PTFE/silicone septa closures were filled with a known mass of sediment and synthetic groundwater designed to mimic typical ionic strength and cation proportions of the sandstone groundwaters in Birmingham (Na<sup>+</sup> 13.0 mg/l; Ca<sup>2+</sup> 72.9 mg/l; Mg<sup>2+</sup> 28.0 mg/l; Cl<sup>-</sup> 149.5 mg/l; SO<sub>4</sub><sup>2-</sup> 110.7 mg/l). Vials were completely filled to prevent volatilisation losses and then spiked with a known mass of PCE and left to equilibrate. After equilibration, PCE concentra-



tions remaining in the aqueous phase were measured and the amount of PCE sorption calculated by difference.

Care was taken to adjust the sediment–water ratio so that predicted sorption (based on  $f_{oc}$ ) would reduce the dissolved concentration by between 20 and 80%, thus reducing the relative error in concentration measurements. PCE stock solutions were prepared by dilution in methanol with spikes below a mole fraction of  $10^{-4}$  in the aqueous phase to avoid co-solvency affects. Each individual experiment to determine sediment sorption at a given concentration was run as a set of three replicates, with one set of vials containing sediment and synthetic groundwater and another two sets containing only synthetic groundwater. One set of blank vials was analysed on the day of spiking to determine initial mass injected, and the other was analysed along with the sorption vials at the end of the equilibration period (3 days) to determine non-sediment sorption mass loss. Day-1 blanks and calibration vials were placed on an orbital shaker table set at 450 motions  $\text{minute}^{-1}$  for 30 min before analysis. Day 3 blanks and sorption vials were placed on a shaker table shaking at 100 motions  $\text{minute}^{-1}$  for 3 days. Vials were centrifuged at 2500 rpm for 30 min prior to extraction of the equilibrated aqueous-phase. PCE concentration was determined by head-space GC–MS.

Batch-sorption tests were performed on: 6 sediment samples taken from two cores from the rural Tern site, with each sample split to 3 sub-samples to evaluate repeatability; on 6 samples taken from two multilevel (ML) core sites on the urban Tame with each sample split to 6 sub-samples; and 6 grab samples from two urban Tame sites ('pebbly sand' and 'hummock sediments'), again each sample split to 6 sub-samples. A single concentration 'spot-wise' sorption  $K_d$  was determined on each sub-sample from an initial spike dissolved-phase concentration of c. 800  $\mu\text{g/l}$  PCE. The value was selected to allow common comparison on samples and multiple sub-samples at a moderately elevated concentration of regulatory concern within a discharging plume and was comparable to higher TCE concentrations at the Tame site); an approach that is acknowledged to not permit investigation of sorption linearity, proposed in future work. PCE diffusion into and through the vial septum was deemed the most significant non-sorption mass loss that was quantified via the sediment-free control vials spiked at c. 8, 80 and 800  $\mu\text{g/l}$  PCE concentrations. Septum mass loss was calculated from the equilibrium (rather than initial) concentrations, similar to Allen-King et al. (1995) following their observation that equilibration of that loss occurs rapidly. This loss was subtracted from the initial mass injected into the vial to calculate a new initial mass ( $M'_0$ ). Sorption was then calculated using (Allen-King et al., 1995):

$$q = \frac{[M'_0 - (C_w V_w)]}{m_s} \quad (1)$$

where  $q$  is the sorbed concentration [ $\text{MM}^{-1}$ ],  $C_w$  is the aqueous equilibrium concentration,  $V_w$  is the volume of water and  $m_s$  is the dry mass of solids. It is acknowledged that assigning losses to diffusion into the septum may be disputed if sorption to substrates is very rapid and the main sink (our sorption parameter estimation is hence regarded conservative, but recognises a future work preference for glass-ampoule based batch sorption measurements to avoid such uncertainties). The sorption (soil–water) partition coefficient,  $K_d$  [ $\text{L}^3\text{M}^{-1}$ ], was then determined using:

$$K_d = \frac{q}{C_w} \quad (2)$$

Recognising sorption of hydrophobic contaminants occurs principally to organic matter, distribution coefficients may be normalised by the laboratory measured fraction of organic carbon in the sediment ( $f_{oc}$ ) to calculate the organic-carbon – water-partitioning coefficient,  $K_{oc}$  (Karickhoff et al., 1979):

$$K_{oc} = \frac{K_d}{f_{oc}} \quad (3)$$

For the River Tame sediments,  $K_d$  was determined for the 6 grab samples taken from different locations across the river to represent the different sediment types (pebbly sand and hummocks) and another 6 samples taken with depth at two locations within a silty – sandy area of the riverbed that was thought to be a potential location for enhanced NA (ML1). For the River Tern,  $K_d$  samples were selected from different depths of two cores, sub-sectioned based on their lithology.

### 3.3.3. Petrographical characterisation of organic matter

The OM present in three shallow grab samples from the Tame riverbed sediments was petrographically characterised. The work was undertaken by a commercial specialist laboratory, LAOP Consulting and Research, Tübingen, Germany (LAOP) and is based on methodologies described by Jeong et al. (2008), Kiem et al. (2003) and Ligouis et al. (2005). It is necessary for identifying condensed carbonaceous materials (i.e., TACM). For example, Yang et al. (2008a,b) used similar techniques to investigate the transport of coal-derived particle-bound hydrophobic PAHs (polycyclic aromatic hydrocarbons) in floodplain soils.

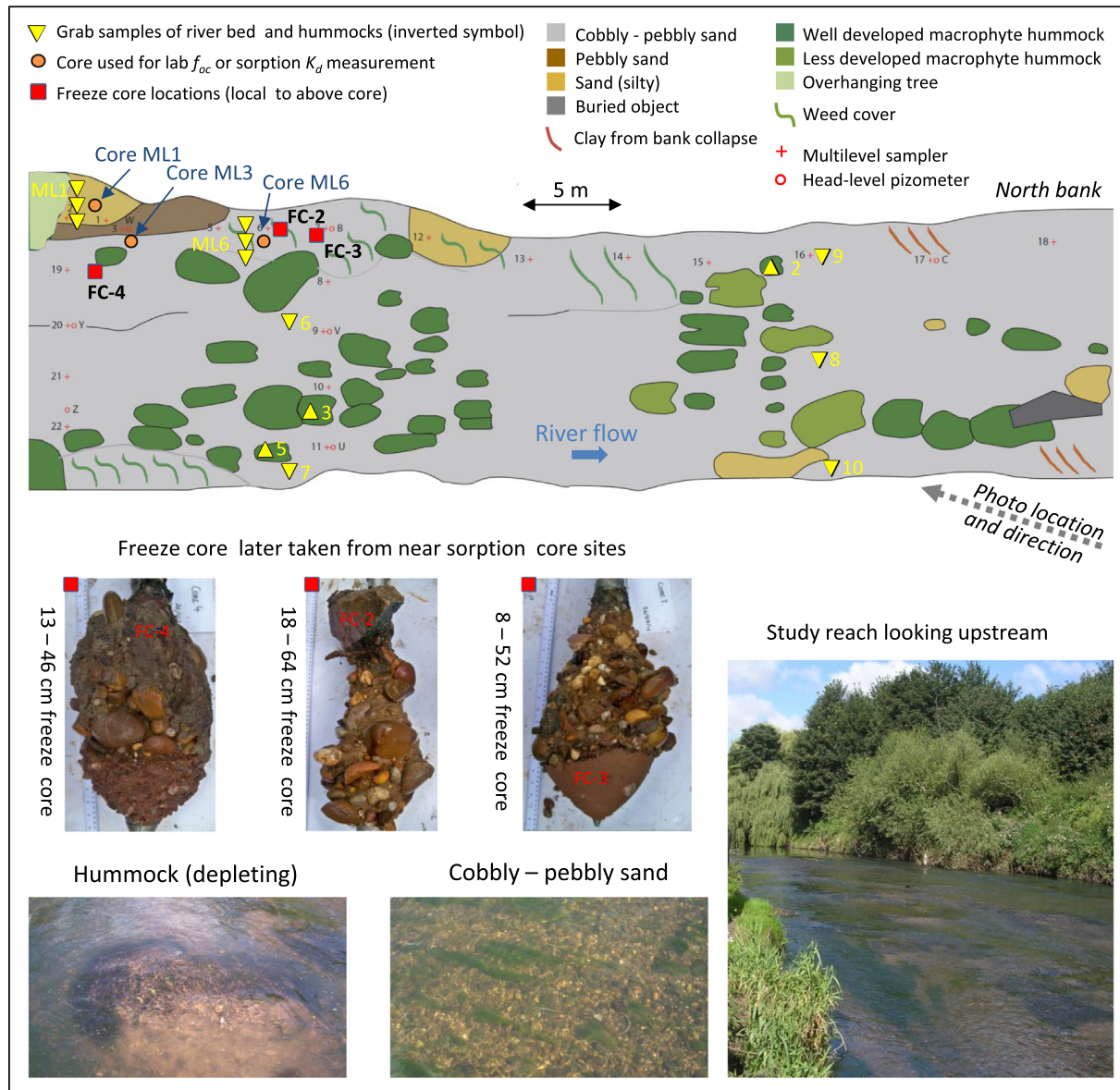
Quantitative microscopical analysis was conducted on polished mounts of organic concentrate produced from HCl and HF acid pre-treatment of 90 g of non-crushed riverbed sediment sample. The analysis was undertaken with a Leitz DMRX-MPVSP microscope photometer in both reflected white-light and UV plus violet-light illumination (fluorescence mode) using an oil immersion objective of 50 $\times$  magnification and a total magnification of 500 $\times$ . Photographs were taken with a Wild MPS48 photoautomat using a 20 $\times$  and a 50 $\times$  oil immersion objective 50 $\times$  (total range of magnification: 200 to 500 $\times$ ). A scale bar of 20  $\mu\text{m}$  or 50  $\mu\text{m}$  is indicated within the images.

The analysis permits a quantitative measure of organic matter type with a broad division between NOM in recent and ancient sediments and AOM as defined earlier.

## 4. Results and discussion

### 4.1. Urban study reach: riverbed inspection

Fig. 2 shows a map of the Tame urban reach riverbed deposits, along with sampling locations and relevant site photographs. The riverbed predominantly comprises a well-armoured cobbly and pebbly sand. However, from spring to autumn, the growth of macrophytes can locally modify the bedform. Hummocks of fine sandy sediments and organic matter build up under trailing strands of macrophytes such as *Ranunculus* due to the reduced water velocities (described by Cotton et al. (2006) for a site elsewhere). Sand hummocks were observed up to several metres in length with thicknesses of up to 50 cm. Their upstream boundaries are curved (Fig. 2, green areas), but downstream areas are actively eroding, with disconnected eddying often including entrained carbon-rich particles. The sand is usually grey or buff in colour, contrasting with the more oxidised appearance of much of the pebbly sand between hummocks, with a centimetre-thick darker rim to the upper surface. In contrast, water flowing around the macrophyte patches is accelerated and flow channels are created where coarser sediments dominate (found elsewhere by Sand-Jensen and Pedersen, 1999). In addition to this increased spatial heterogeneity, the seasonal nature of the macrophyte growth leads to a temporal heterogeneity in sediment structure and retention of organic matter. Even within seasons, the sediment distribution can vary, with hummocks eroding as well as forming (Fig. 2, photograph bottom left).



**Fig. 2.** River Tame 50-m study reach showing mapped near-surface sediments and vegetation alongside core or grab-sample locations and a selection of freeze core and site photographs.

Our grab sediment sampling obtained a representative collection of the ‘hummock sediment’ and the cobbly and pebbly sand. Because the cobbles were discarded after sampling, the cobbly and pebbly sand samples will subsequently be termed the ‘pebbly sand’ samples. Further grab riverbed sampling, but with depth (Fig. 2), was undertaken adjacent to the location of the ML3, ML6 and ML1 cores, the samples obtained being used for determination of  $f_{oc}$  and  $K_d$ . Some of the freeze cores later retrieved from the site (Freitas et al., 2015) are shown in Fig. 2 and illustrate the significant heterogeneity of the riverbed deposits. The cores display an array of poorly sorted deposits, albeit with some layering obvious in places, with grain-size varying from fine silt to cobbles. The observation of barbed wire (in rusted degraded state) at 30 cm below the current riverbed in freeze core FC2 demonstrates the relatively recent age of the deposits sampled for  $f_{oc}$  and  $K_d$  determination. Our infrequent observations spanning around a decade have observed changes in the reach bedform locally due to accumulation of both natural and anthropogenic debris and flood scouring, further indicating the dynamic nature of this urban riverbed environment.

#### 4.2. $f_{oc}$ data

Table 1 summarises  $f_{oc}$  data obtained, comprising a total of 5 cores and 16 grab samples for the urban Tame site and 7 cores for the rural Tern. The data indicate means and ranges for the various sediment types that broadly accord with the relative expectation of  $f_{oc}$  contents for the sediment types sampled. For example, the pebbly sands of the Tame and sands of the Tern have low  $f_{oc}$  values (often <1%), whilst the hummock sediments under the Tame macrophyte stands and the Tern organic rich units have the highest values (up to 21%). For each sediment type the arithmetic mean and geometric mean  $f_{oc}$  are reasonably comparable. The means of ‘All River Tern samples’ is somewhat misleading as the estimates are drawn from two contrasting populations, i.e., low  $f_{oc}$  sands (to which the geometric mean tends) and high  $f_{oc}$  organic-rich units (to which the arithmetic mean tends).

The mean  $f_{oc}$  values for the various sediment types (Table 1) are generally within, or approaching the range reported by Clarke and Wharton (2001) for other lowland English rivers (0.6 to 9.1%). Observed riverbed  $f_{oc}$  values are much larger than adjoining aquifer

**Table 1**Summary of riverbed sediment  $f_{oc}$  data for the urban River Tame and rural River Tern sites.

| Sediment type                                     | Min $f_{oc}$<br>% | Max $f_{oc}$<br>% | Arithmetic mean $f_{oc}$<br>% | Standard Deviation<br>% | Geometric mean $f_{oc}$<br>% | n  |
|---|-------------------|-------------------|-------------------------------|-------------------------|------------------------------|----|
| Pebbly sand, River Tame                           | 0.29              | 1.71              | 0.85                          | 0.45                    | 0.743                        | 16 |
| Silty sand, River Tame                            | 0.76              | 6.42              | 3.18                          | 1.59                    | 2.75                         | 16 |
| Hummock sediment sub-macrophyte stand, River Tame | 0.86              | 6.24              | 3.24                          | 2.34                    | 2.28                         | 4  |
| All River Tame samples                            | 0.29              | 6.42              | 2.15                          | 1.78                    | 1.51                         | 36 |
| Sand, River Tern                                  | 0.06              | 5.89              | 1.11                          | 1.35                    | 0.722                        | 50 |
| Organic rich unit, River Tern                     | 4.63              | 20.60             | 12.84                         | 5.48                    | 11.46                        | 19 |
| All River Tern samples                            | 0.06              | 20.60             | 4.28                          | 5.88                    | 1.43                         | 75 |

values. The Triassic sandstone that underlies both the Tame and Tern exhibits a typical range of 0.01 to 0.15% (Steventon-Barnes, 2001; Thornton et al., 2000; Shepherd et al., 2002). The riverbed deposit  $f_{oc}$  values are hence 1 to 2 orders of magnitude greater than the sandstones and confirm the general expectation, given a preliminary assumption similar  $K_{oc}$  values apply, of much greater retardation occurring in the riverbed sediments.

Vertical profiles of Tame riverbed indicate  $f_{oc}$  was quite elevated at 0.5 to 7% (Fig. 3). The core profiles, which cover a depth interval from 0 to 20–25 cm below the riverbed, show some significant differences despite their relative proximity (Fig. 2). ML6 has low  $f_{oc}$  throughout (c. 0.6%) whilst both ML1 and ML3 exhibit higher values declining with depth (from 4% to 2%, and 6.5% to 1.5%, respectively). The shallowest (0–10 cm depth) ML1 sample is described as soft brown-grey fine grained sand and silt with visible organic matter particles present that are well-degraded and dark brown-black in colour as well as some woody debris. This contrasts with the shallowest ML6 sample described as mainly pebbles (60%) with medium-coarse grained brown sand and gravel and no visible organic matter.

The 2-cm increment ML3 data illustrate the  $f_{oc}$  heterogeneity. Whilst not all high  $f_{oc}$  strata are always obvious visually, the organic-rich unit seen at 10–15 cm depth in the photo-log of ML3 in Fig. 3 corresponds with the  $f_{oc}$  7% peak. This compares to

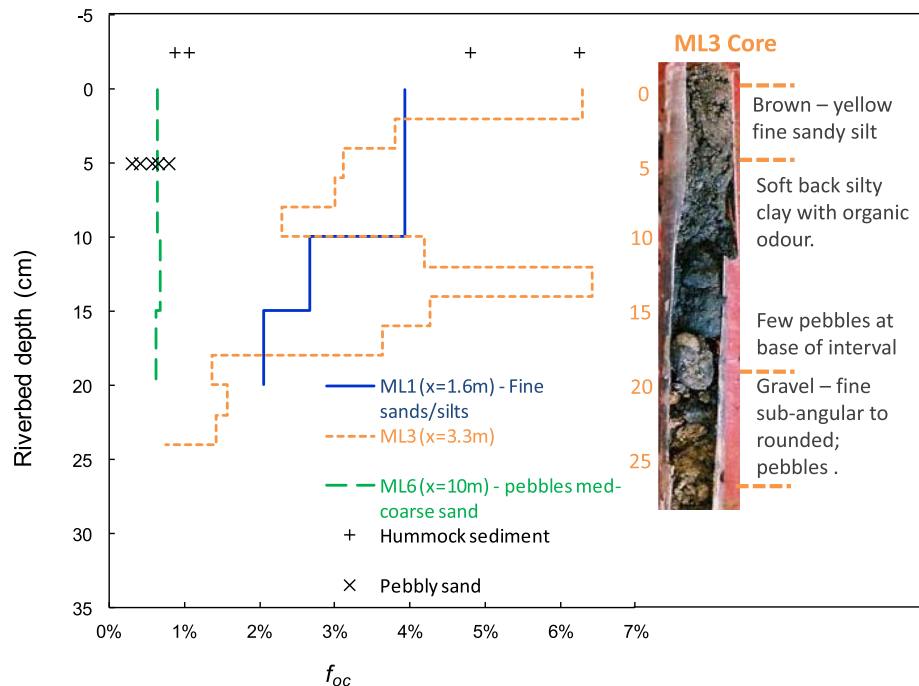
the shallow pebbly sand grab samples (Table 1) with little obvious organic content that had  $f_{oc}$  values of 0.3 to 1.7% and arithmetic and geometric means of around 0.8%. This sample material (with cobbles removed) represents the very shallow armoured pebble – cobble deposit evident across much of the reach (see Fig. 2, incl. photograph). Samples of hummock sediment exhibited  $f_{oc}$  spanning the riverbed range (1–6%; Table 1); the field description of the 6% sample included “visible well degraded consolidated organic matter as well as larger fragments of organic detritus”. The  $f_{oc}$  range accords with our observation of organic-rich (rims especially) and less organic parts of the hummocks, and also sand-sized particles of coal-like material deposited in the eddying downstream wakes of the hummocks.

The rural Tern core samples used subsequently for laboratory determination of  $K_d$  were from the mid to high range of  $f_{oc}$  values (Table 1): for Core 1, 7%, 15%, 19% and 6%; and for Core 2, 15% and 16% (with increasing depths). These samples are organic-rich units of what appear to be relatively recent depositional origin.

#### 4.3. PCE batch sorption studies

##### 4.3.1. $K_d$ and $K_{oc}$ estimates

Results of the PCE batch sorption studies are summarised in the Fig. 4 plot of experimentally observed sample  $K_d$  values versus  $f_{oc}$ ,



**Fig. 3.** Fraction of organic carbon ( $f_{oc}$ ) variation in Tame riverbed core and grab samples. Depths are shown below riverbed at sample locality except for the hummock sediment samples plotted at an arbitrary negative depth reflecting their position above the wider riverbed.



gradients representing the sediment  $K_{oc}$  (Eq. (3)). An approximately linear increase of  $K_d$  with  $f_{oc}$  was observed for each sample type, except ML6 that showed too little variation in  $f_{oc}$  to make a meaningful evaluation in this regard.  $K_{oc}$  was greatest for sample ML1 at 7370 l/kg corresponding to a fine-grained sand and silt, a softer sediment area below an overhanging tree partially protected from the main river flow (Fig. 2). Whilst the pebbly sand has a low  $f_{oc}$  compared to some of the high  $f_{oc}$  hummock sediments, data for both display similar gradients in Fig. 3 with comparable  $K_{oc}$  calculated of 1530 l/kg and 1950 l/kg.  $K_{oc}$  similarity suggests these sediments, both from the shallow riverbed (and certainly very recently deposited in the case of the hummock samples), contain similar organic material.

Fig. 5 shows calculated  $K_{oc}$  values (Eq. (3)) plotted against  $f_{oc}$  for the urban Tame and rural Tern samples, including sub-sample (open symbol) and mean sample (filled symbol) estimates. Discussion below focuses upon the mean data, but noting that sub-sample variation is shown to be least for the ML1 and ML6 Tame riverbed core with a standard deviation of 5.59% of the mean, compared to 15.5% for the rural Tern samples and 24.3% for the pebbly sand and hummock Tame samples. The Fig. 5 plot adopts a similar format to the second figure in Wang et al. (2013), including reference  $K_{oc}$  lines for the US EPA (1996) geometric mean (265 l/kg) alongside empirical solubility and  $K_{ow}$  (octanol–water partition coefficient) based estimates of  $K_{oc}$ . These latter estimates are calculated using the approach of Wang et al. (2013), derived from linear solvation energy or hydrophobic partitioning theory (Schwarzenbach et al., 2003). With the exception of some pebbly sand samples, all of the Tame riverbed sample  $K_{oc}$  mean estimates are at least double the US EPA (1996)  $K_{oc}$  at over 500 l/kg with most samples over 1000 l/kg. The  $K_{oc}$  values for the low  $f_{oc}$  content ML6 samples are elevated at c. 2000–4000 l/kg, approaching the maximum study values of c. 7000 l/kg found for ML1.

In contrast to the elevated urban sample  $K_{oc}$  values, Fig. 5 shows a clustering of the rural River Tern samples close to the US EPA geometric mean. Tern data for cores 1 and 2 have sample-based  $K_{oc}$  arithmetic and geometric means of 241 and 245 l/kg respectively. Drawing on the discussion of Wang et al. (2013), the US EPA geometric mean of 265 l/kg is expected to be valid when applied to modern sediments that have quite high  $f_{oc}$  and/or when high PCE concentrations tending to solubility are present (studies that contributed to the US EPA value tended to accord with these criteria). Under these conditions, absorption partitioning is domi-

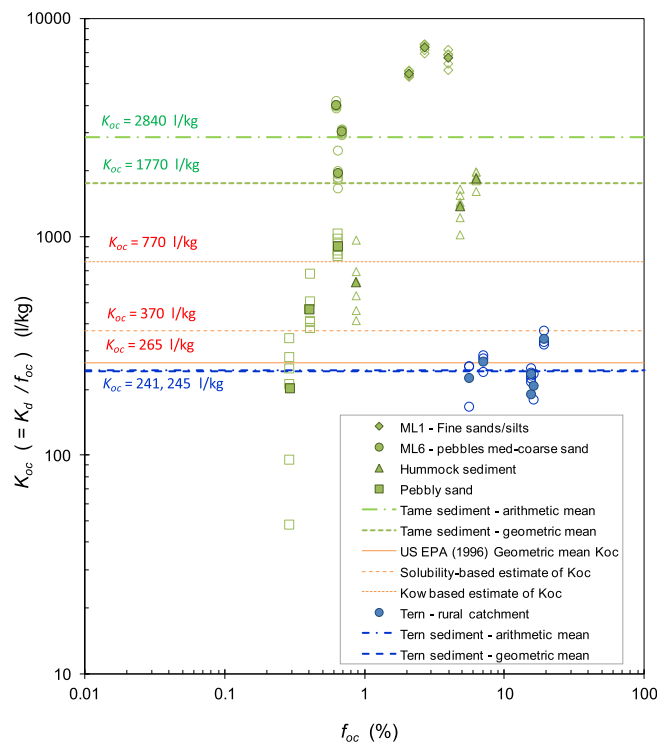


Fig. 5. Plot of calculated  $K_{oc}$  versus sample  $f_{oc}$  for Tame (urban) and Tern (rural) riverbed sediment samples shown relative to various sample mean and literature  $K_{oc}$  estimates. Sub-sample data are shown as open symbols of similar shape and colour to their mean sample, filled symbol, estimates. The plot may be directly compared to Figure 2 of Wang et al. (2012).

nant since any of the limited adsorption sites will have become saturated. The US EPA value compares well to the  $K_{oc}$  derived from both solubility and  $K_{ow}$ . This consistency endorses the US EPA value for sediments where absorption partitioning is dominant for PCE. It is concluded from the similarity of the Tern sample  $K_{oc}$  estimates with the US EPA  $K_{oc}$  estimates that absorption is predominant. This is entirely reasonable based on the fact that the rural Tern samples are unlikely to contain significant quantities of TACM and are likely to be dominated by recent NOM.

Unlike the rural sediments, most of the urban sediments have  $K_{oc}$  estimates well above the US EPA mean (Fig. 5), providing strong evidence of adsorption contributions. Our urban  $K_{oc}$  values are similar to the PCE estimates of Wang et al. (2013) that show that the majority of TACM-samples plot in the 1000–10,000 l/kg  $K_{oc}$  range (comparing to Wang et al.'s Figure 2a,b plots of 5 and 5000  $\mu\text{g/l}$  PCE data bracketing our concentrations). We conclude our urban riverbed sediments exhibit significant and varying adsorption contributions that are highly likely to be attributable to the variable presence and, or type of TACM. Due to the variability in the urban  $K_{oc}$ , calculated arithmetic and geometric mean  $K_{oc}$  values for all the urban Tame data of 2840 and 1770 l/kg respectively somewhat differ (Fig. 5). Greater sample numbers are necessary to more fully comment on the statistical nature of the urban distribution.

#### 4.3.2. R estimates

Fig. 6 plots calculated retardation factor,  $R$ , estimates for PCE from the batch  $K_d$  data as a function of sediment  $f_{oc}$  based on the standard relationship:

$$R = 1 + \frac{\rho_b K_d}{\eta} \quad (4)$$

where  $\rho_b$  is the dry-bulk density of the sediment and  $\eta$  its porosity to which nominal representative values are respectively allocated of 1.855 kg/l and 0.3. Reference  $R$  lines are calculated for the sample

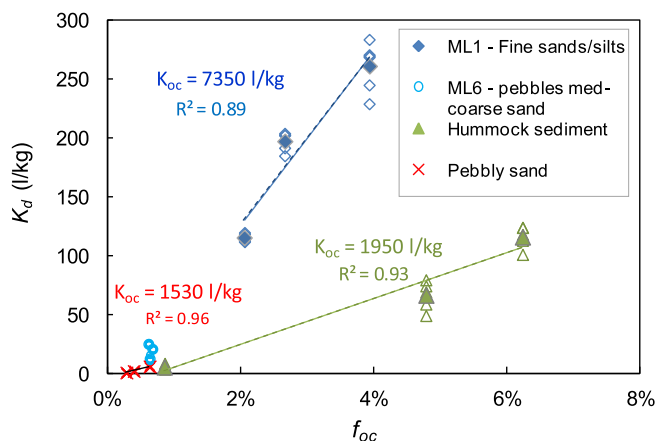


Fig. 4. Laboratory PCE  $K_d$  estimates for Tame samples plotted against  $f_{oc}$  with calculated linear best fit lines of gradient  $K_{oc}$  (Eq. (1)). Sub-sample estimates for the ML1 and hummock sediment datasets are shown as open symbols of similar shape and colour to their mean sample, filled symbol, estimates.



arithmetic and geometric means of the Tame and Tern data and for the US EPA geometric mean  $K_{oc}$ .

Point  $K_d$  mean and the trend-line for the rural Tern data lie very close to the US EPA estimate (Fig. 6);  $R$  ranges from 80 for the low  $f_{oc}$  (5.5%) up to 400 for the maximum  $f_{oc}$  (19%). The only Tame sample close to the US EPA trend-line is a pebbly sand sample. This yields the study minimum  $R$  of just 4.6 arising from its low  $f_{oc}$  (0.3%). These  $R$  estimates relate to sediments where sorption appears to be dominated by absorption to recent NOM. The agreement supports that use of the US EPA geometric mean  $K_{oc}$  combined with a measured Tern riverbed  $f_{oc}$  should provide a reliable prediction of retardation occurring in these rural riverbed sediments. The geometric mean for the full Tern  $f_{oc}$  dataset generates an  $R$  estimate of 24. The arithmetic mean, influenced by some elevated  $f_{oc}$  values, realises an  $R$  of 71 and the maximum Tern  $f_{oc}$  yields an  $R$  of 340. The variation is illustrative of the sensitivity of retardation to the magnitude and spatial variability of  $f_{oc}$  within the riverbed. By way of comparison, the Triassic Sandstone aquifer  $f_{oc}$  range reported earlier of 0.01 to 0.15% generates very low  $R$  estimates of 1.2 to 3.5. PCE velocities through the rural Tern riverbed sediments are hence 1 to 2 orders of magnitude lower than those in the adjoining sandstone aquifer.

It is obvious from Fig. 6 that the US EPA  $K_{oc}$  forms a very poor basis for the prediction of the observed  $R$  estimates for the urban samples. It would generally lead to very significant underestimation of the urban sample  $R$ . The seven samples that have  $f_{oc}$  in the range 0.3 to 0.9% are illustrative of the poor predictability of  $R$  from  $f_{oc}$  data using a single literature  $K_{oc}$ . The US EPA  $K_{oc}$  would predict  $R$  in the range 6 to 16 for these sediments, yet actual  $R$  estimates from laboratory  $K_d$  data range from 4.6 to 155. The arithmetic and geometric mean Tame sediment  $R$  lines are around an order of magnitude above the US EPA estimate. The greatest  $R$  values for the ML1 samples, which had a moderate  $f_{oc}$  of 2 to 4% (less than Tern samples), were estimated at 715 to 1620 for which the US EPA trend-line would have returned  $R$  values of 34 to 67.

The underestimation of  $R$  when using the US EPA  $K_{oc}$  values suggests a greater degree of sorption, an observation consistent with the presence of TACM. Review of all the urban points in Fig. 6 is suggestive of a broadly increasing  $R$  with increasing  $f_{oc}$  emerging from lower values of  $f_{oc}$  and  $R$  being relatively close to US EPA trendline. This observation is the basis of using a simple mixing

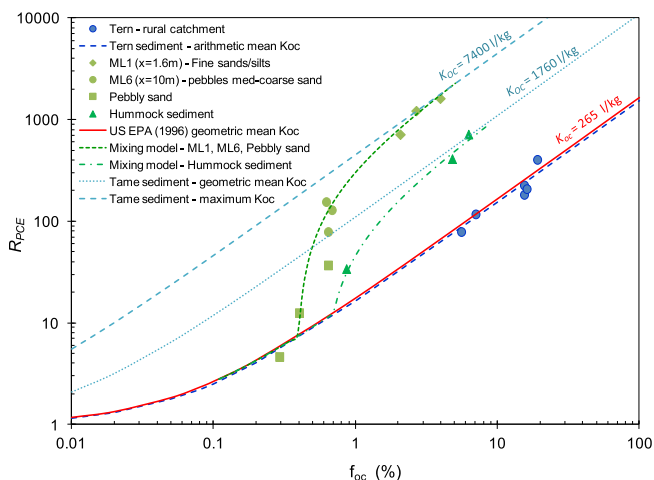
model to describe the relationship whereby sorption is assumed to occur to a mix of recent NOM and TACM. Sorption to the NOM proportion of the  $f_{oc}$  is characterised by assuming the US EPA  $K_{oc}$  applies and to the remaining proportion of TACM of the  $f_{oc}$  that the  $K_{oc}$  observed to fit the maximum  $f_{oc}$  values applies. A mixed  $K_d$  may hence be calculated and substituted into Eq. (4) to calculate the trend in  $R$  with  $f_{oc}$  based upon:

$$K_d = f_{oc-NOM}K_{oc-NOM} + f_{oc-TACM}K_{oc-TACM} \quad (5)$$

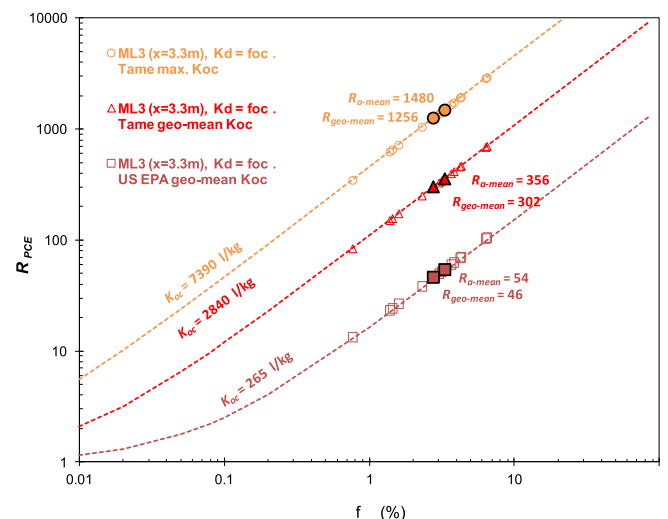
Two mixing relationship lines are shown in Fig. 6 that encompass the urban samples. A lower line approximately fits the hummock sediment samples and assumes  $f_{oc-NOM}$  is fixed at 0.7% (point of departure from the US EPA trend-line) and  $f_{oc-TACM}$  fully accounts for the increased  $f_{oc}$  value above this point with the  $K_{oc-TACM}$  assumed to be 1800 l/kg and is close the Tame geometric mean  $K_{oc}$ , also plotted to which it approximately converges. The higher mixing line that approximates the deeper riverbed more sorbing ML1 and ML6 sediment samples assumes a fixed  $f_{oc-NOM}$  of 0.4% and a  $K_{oc-TACM}$  of 8000 l/kg that provides an estimation of the  $K_{oc}$  applicable to the TACM. Whilst it is arguable as to the assigned  $f_{oc}$  proportions (the  $f_{oc-NOM}$  may be underestimated), the mixed line profiles do nevertheless provide a valid descriptor of the observed urban  $R$  variations.

Fig. 7 adopts a similar style to Fig. 6, but focuses on the ML3 dataset for which only  $f_{oc}$  (and no  $K_d$ ) data were obtained (Fig. 3). Various  $K_{oc}$  can be assigned to estimate a  $K_d$  and  $R$ . The figure shows trend-lines for  $R$  and the individual ML3 data points that reflect the  $f_{oc}$  variability in the core based on: i) the US EPA (1996)  $K_{oc}$  representing an absorption dominated sediment; ii) geometric mean urban Tame  $K_{oc}$ ; and, iii) maximum urban Tame  $K_{oc}$ . Within each of these estimates the arithmetic and geometric mean  $R$  estimates for the ML3 profile are highlighted. The plot illustrates the vast range in  $R$  that may result for these different, bounding,  $K_{oc}$  assumptions. It highlights not only the greater than an order of magnitude variation in  $R$  that may result from different selection of  $K_{oc}$ , but also for a given  $K_{oc}$ , that the range in  $R$  also approaches an order of magnitude due to the variability of  $f_{oc}$  (cf. Fig. 3). The absence of any ML3  $K_d$  data is a significant handicap to confidently predicting the riverbed deposit properties here: the prudent choice would probably be the selection of the geometric mean Tame urban  $K_{oc}$ .

Retardation of the lesser chlorinated CAHs, often present at sites including the study site (Freitas et al., 2015), will be reduced com-



**Fig. 6.** Plot of Tame (urban) and Tern (rural) riverbed calculated PCE retardation factor  $R$  (Eq. (4)) versus  $f_{oc}$  for sample point and various mean and maximum Tame and Tern  $K_{oc}$  data estimates. Calculated mixing model lines based on Eq. (5) detailed in the text are shown to reasonably describe the urban Tame data.  $R$  calculated from the US EPA (1996) geometric mean  $K_{oc}$  is shown for reference.



**Fig. 7.** Plot of Tame ML3 riverbed sample calculated PCE retardation factor  $R$  versus  $f_{oc}$  for various  $K_{oc}$  assumptions.

pared to PCE due to their lower hydrophobicity and sorption potential. As a first approximation, indicative  $R$  (or  $K_d$  or  $K_{oc}$ ) estimates may be generated based on solubility scaling methods (as used by Rivett and Allen-King (2003)) to account for their reduced hydrophobicity. TCE is around a factor of 5 and cDCE (cis-dichloroethene) and VC (vinyl chloride) around an order of magnitude more soluble than PCE.  $R$  estimates for the lesser chlorinated CAHs may be anticipated to be reduced by around these factors as a crude first estimate. Relative sorption may also be made from studies examining sorption for several CAH. For example, Lu et al. (2011) provide  $K_d$  for the above CAH on clayey tills that approximately scale with hydrophobicity commensurate with the above expectations (noting their dataset  $f_{oc}$  (0.02–0.08%) and PCE  $K_d$  (0.84–2.45 l/kg) are around the minima of data reported herein).

#### 4.4. Organic petrography

The three shallow grab samples from the Tame riverbed sediments examined using organic petrographic techniques (LAOP) were obtained from deposits with the following characteristics:

- a brown-grey fine grained 'ML1 sand' and silt with Visible OM fragments present such as leaves and woody debris, less well degraded than found in the upper 10 cm (sample ML1 (10–15 cm));
- a brown-grey, fine-medium grained hummock sand and silt with visible well degraded consolidated OM as well as larger fragments of organic detritus (grab sample 5);
- a yellow-brown 'pebbly sand' from the armoured riverbed, with 'No visible OM' (grab sample 8).

Before organic petrographic examination, any large clasts, organic or otherwise, were removed from the sample, leaving the granular matrix. This procedure avoided the possibility of, for example, a large woody fragment dominating any given sample.

Table 2 summarises the much more detailed tabulation of data provided by LAOP. The table subdivides to the general categories of recent NOM and AOM, the latter includes significant TACM. It may be construed arguable as to whether all items under AOM are truly anthropogenic. For example, 'hard coal' variously elevated in Table 2 samples may potentially have some natural 'geogenic' origin arising from river or run-off erosion of near-surface coal seams. Most seams will, however, be either protected by alluvial or glacial sediments within or near the Tame, or else mined long ago due to their shallowness and ease of access. Coal-related OM found in the riverbed has much more likely arisen from coal particle release associated with the recent centuries of intense mining operations, spoil tip leaching and abandoned workings and rebounding mine-water overflows as well as more general industrial/urban anthropogenic activity. Although a rural catchment overlying Coal Measures may provide a more rigorous background comparator to assess relative influence of anthropogenic versus geogenic natural release of coal particles, most, if not all such catchments in the UK are highly urbanised and extensively mined.

Table 2 confirms that the proportion of NOM within the greater sediment OM was small, ranging from 5.2 to 14.7% with the majority being gelified or non-gelified woody phytoclast material (tissues & structureless humic detritus). The hummock sand sample is almost certainly negatively biased as larger OM fragments (described above) were omitted and the sample largely reflects the macrophyte-filtered riverine sediment.

All sediments are dominated by the AOM, comprising 85–95% of the OM (Table 2). Nearly all types of anthropogenic particles in LAOP's classification system were found to be present suggesting a diversity of OM input to the Tame. The principal sources of the OM particles found appear to be from coal mining or coal process-

**Table 2**

Organic matter (OM) composition (% by weight) of selected Tame riverbed sediment samples as determined by organic petrography. The  $f_{oc}$  of the sediment sample subsampled for organic petrography analysis is indicated.

|  | Hummock sand     | Pebbly sand      | ML1 sand         |
|--|------------------|------------------|------------------|
|  | $f_{oc} = 6.2\%$ | $f_{oc} = 0.4\%$ | $f_{oc} = 2.7\%$ |
|  | %                | %                | %                |
| <b>Recent natural organic matter (NOM)</b>                             | <b>5.2</b>       | <b>8.5</b>       | <b>14.7</b>      |
| Non-gelified woody phytoclast (tissues & structureless humic detritus) | 2.2              | 7.8              | 2.3              |
| Gelified woody phytoclast (tissues & structureless humic detritus)     | 3                |                  | 12.4             |
| Seed coatings  | X                | 0.3              |                  |
| Suberized tissues (bark, root)   | X                |                  | X                |
| Fungal phytoclast  |                  | 0.4              | X                |
| <b>Anthropogenic organic matter (AOM)</b>                              | <b>94.8</b>      | <b>91.5</b>      | <b>85.3</b>      |
| Raw brown coal   | 1.8              | 0.9              | 1.8              |
| Hard coal  | 53.4             | 28               | 33               |
| Charcoal (recent & fossil)   | 1.1              | 4.2              | 0.6              |
| Coke carbon forms (hard coal carbonization)                            | 10.7             | 11.1             | 5.8              |
| Petroleum coke (carbonization)   | –                | 0.2              | X                |
| Residues of coal hydrogenation   | 22.8             | 37               | 30.5             |
| Char (solid residues of coal combustion, coal liquefaction)            | 3.6              | 1.2              | 9.2              |
| Soot (traffic soot, soot from oil combustion)                          | ?                | ?                | ?                |
| Coal and petroleum derived fluorescent materials                       | 1.4              | 8.9              | 4.4              |
| Graphite   | –                | x                | –                |

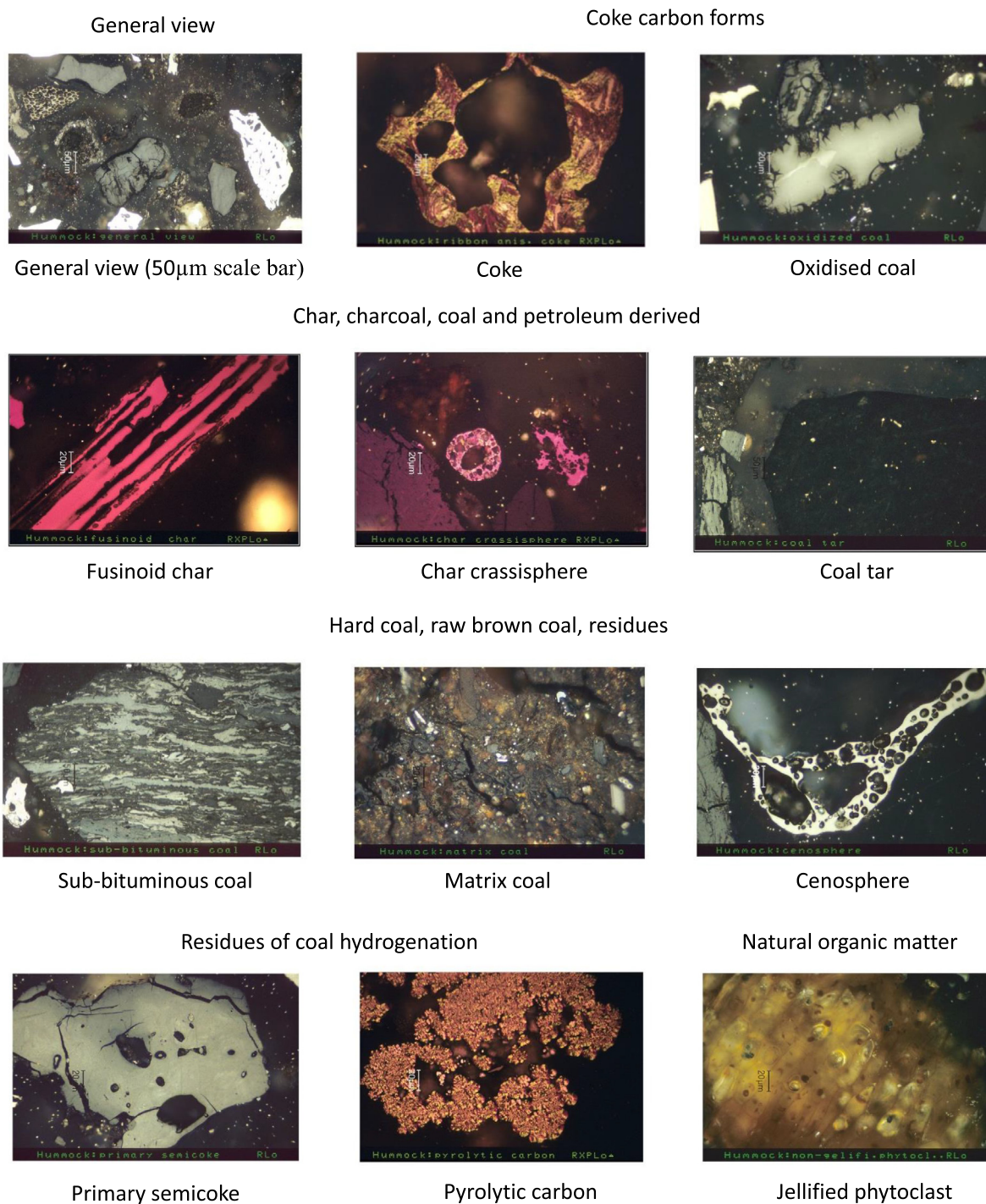
x: present but not expressed as percentage due to scarcity; ? soot was counted together with residues of coal hydrogenation due to similarity in structure.

ing (cokes; residues and solids produced during coal hydrogenation processes). Hard coal accounts for 28–53% alongside high levels of residues of coal hydrogenation at 23–37%. Contribution to the former from natural erosion of coal is possible, but likely very limited relative to the anthropogenic mediated contribution from the historic coal mining activity (Parker, 2015). The residue percentages are probably an overestimate (Table 2 footnote) as they also include soot from traffic and oil combustion, which are likely to be present due to the high density of major and minor roads in the vicinity of the river. There is some evidence of coal- and petroleum-derived fluorescent materials at 1–9%. These will include tar, oils and lubricants; the greatest quantity being found in the pebbly sand, i.e. the shallow armoured riverbed deposit.

A selection of petrographic images is shown for the hummock and pebbly sand samples in Fig. 8 and Fig. 9 (see Crelling and Rimmer (2015) for relevant terminology). These, again, are from a database of many images provided by LAOP and are selected to provide an illustration of the diversity of OM types encountered (but do not provide comprehensive coverage). With the exception of the lower right images in both figures of NOM examples, the other images illustrate the diversity of the TACM-dominated organic matter – AOM found. The images cover various forms of coal, coke, char and soots. Added to these are several images of (coal) tar, a viscous NAPL produced in the past at town gas or coal carbonisation works (aka. manufactured gas plants), not infrequently located in the vicinity of rivers (or canals) and a key target of land remediation programmes in the past two decades. The size of most anthropogenic particles observed is relatively large and is speculatively ascribed to potentially short transport distances from the sources. Most of the coal particles are described as very "fresh" with limited or no weathering.

The above observations are consistent with the catchment's mining-related industrial past (Section 2.1). The organic petrography confirms the predominance of AOM over NOM. In addition, it

## 'Hummock' urban riverbed sediment samples



**Fig. 8.** Selection of images obtained from organic petrography analysis of the 'Hummock' urban riverbed Tame sediment samples.

demonstrates the significant occurrence of TACM, essential to the argument of [Section 4.3.2](#) that the sorption properties observed are due to the presence of anthropogenic carbon. The diversity of OM shown by the images ([Figs. 8 and 9](#)) in particular highlight that TACM-based sorbents in the urban environment are heterogeneous with solid particulate and even liquid (NAPL) phases present of contrasting size, surface area, surface nature and anticipated microporosity of some TACM.

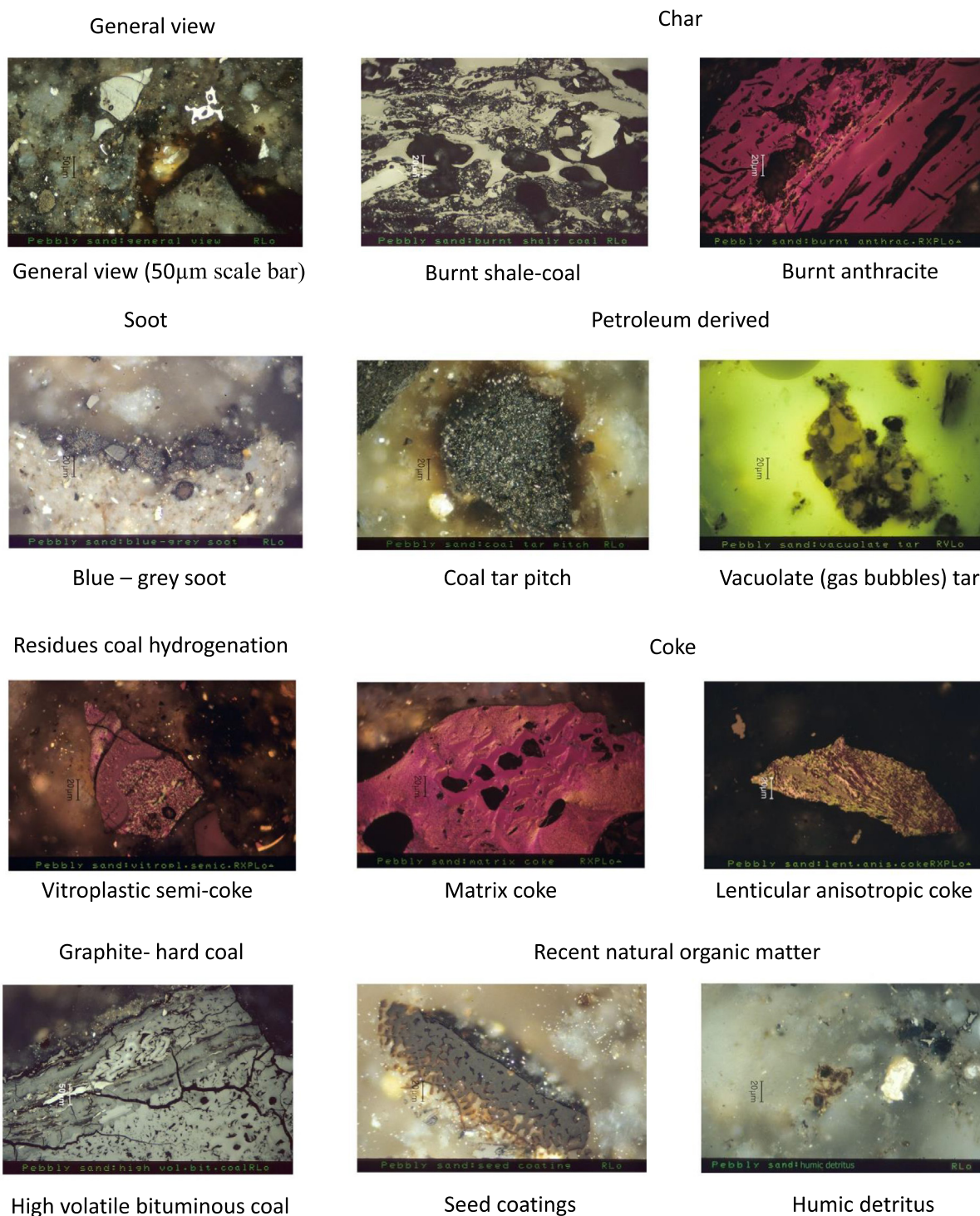
## 5. Illustrative modelling to explore implications

### 5.1. Approach

To investigate the implications of the modified description of riverbed sediment sorption, some illustrative modelling has been undertaken using PCE as the example contaminant. The aims of the work were to investigate the residence time effect on NA using



## 'Pebbly sand' urban riverbed sediment sample



**Fig. 9.** Selection of images obtained from organic petrography analysis of the 'Pebbly sand' urban riverbed Tame sediment samples.

our revised understanding of sorption behaviour in urban riverbed deposits.

For the modelled riverbed sections a common porosity and groundwater flux was specified. Dissolved-phase PCE solute was injected continuously. The selected flow and transport parameters are given in Table 3. These values are appropriate for saturated groundwater discharge from an underlying aquifer up into a river, as encountered in the Tame and the Tern. The values are based on

data obtained for the study site (Freitas et al., 2015) and the greater reach study by Ellis and Rivett (2007).

The layered heterogeneity of  $K_d$  is represented directly for the urban Tame cores ML1 and ML6 based on the profile data presented in Fig. 3. A similar approach is taken for the rural Tern core 1, with  $K_d$  data for 4 discrete intervals. The urban Tame core ML3  $f_{oc}$  results (13 discrete intervals, Fig. 3) were used as a basis for illustrating the sensitivity of residence times to  $K_{oc}$  selection: arith-



**Table 3**

Parameters used for modelling PCE plume transport through various riverbed core.

| Parameter                 | Symbol    | Value     | Units | Comments   |
|---------------------------|-----------|-----------|-------|--|
| Hydraulic conductivity    | $K$       | 1         | m/d   | Not an untypical riverbed mean $K$ for the Tame riverbed literature of range $\sim 0.01$ – $10$ m/d                      |
| Hydraulic gradient        | $i$       | 0.03      | –     | Typical head differences in riverbed of 1 to 2 cm or so over 50 cm   |
| Porosity                  | $n$       | 0.3       | –     | Nominal value for riverbed sediments   |
| Pore velocity             | $v$       | 0.1       | m/d   | Darcy's Law calculation from above parameters  |
| Path-length               | $L$       | 0.19–0.28 | m     | Riverbed thickness – value taken to be core length   |
| Dispersivity              | $\alpha$  | $0.1 * L$ | m     | 10% of path-length (a standard assumption)   |
| Sediment dry bulk density | $\rho_b$  | 1.855     | kg/l  | Calculated from $n$ and particle density of 2.65 kg/l  |
| Retardation factor (PCE)  | $R$       | 13–2598   | –     | Calculated via Eq. (4) directly using $K_d$ or calculated $K_d = f_{oc} * K_{oc}$ from core interval data (e.g., Fig. 3) |
| Half-life (PCE)           | $T_{1/2}$ | 10–1000   | d     | Illustrative range: 10 d, 100 d, 1000 d and no decay   |

metric average  $K_{oc}$  values from the Tern core 1 (269 l/kg), similar to the US EPA (1996) geometric mean, and from the Tame (2844 l/kg) were used.

The conventional advection–dispersion–retardation–degradation approach was used with a linear equilibrium isotherm  $R$  (Eq. (4)). Biodegradation sensitivity was assessed through a range of nominal degradation rates (half life: 10, 100, 1000 d and no decay), reflecting the site-specific nature of biodegradation. Model runs were undertaken to evaluate bioavailability influence by assuming: i) biodegradation only occurred when in the dissolved phase (i.e., the sorbed-phase contaminant was not bioavailable); and ii) biodegradation occurred in both dissolved and sorbed phases. Case i) was accomplished simply by scaling the aqueous half-life by  $R$ . Case ii) is recognised as probably not realistic, but nevertheless permits simulation of a maximum degradation extreme scenario.

There are no exact solutions for the layered system even in 1-D and so either numerical modelling or semi-analytical approaches are required. A numerical modelling approach would be computationally intensive to ensure fully converged solutions. We have instead used a Laplace transform approach with numerical inversion of the solution to the resulting ordinary differential equation (ODE) (Robinson and Hodgkinson, 1987). We have evaluated the solution at the end of the sediment core profile for selected times to construct the breakthrough curve. The inversion is accomplished using Talbot's (1979) method, utilising his recommended contour shape parameters and ensuring convergence of the integration scheme by checking a 128 point integration scheme against the 64 point solution used.

Each discrete section in the profile can be solved in Laplace transform space simply as a second-order ODE with an exponentially growing and declining term. We select the exponentially declining term which is suitable for the requirement that concentration would tend to zero at infinity in a semi-infinite section. The output flux from each layer is passed as the inlet flux to the subsequent layer, and the output flux from the final layer converted back to a concentration. This leads to an extremely efficient scheme for simulating layered heterogeneous one-dimensional systems. It does not allow for back dispersion between adjacent sections which is not unphysical for systems such as considered here where concentration gradients are always negative. The approach is implemented in an Excel spreadsheet tool using Visual Basic for Applications (VBA) for the function evaluations in s-space and the numerical integration in the complex plane (Case, 2014).

### 5.2. Simulations evaluating sorption influence upon residence times

The contrast between urban (Tame) and rural (Tern) riverbed deposit PCE sorption behaviour is illustrated in Fig. 10. All simulations adopt a half-life of degradation of 10 d that is only active when the contaminant is present in the dissolved-phase. Simulated profiles with symbol markers are for the riverbed core having labo-

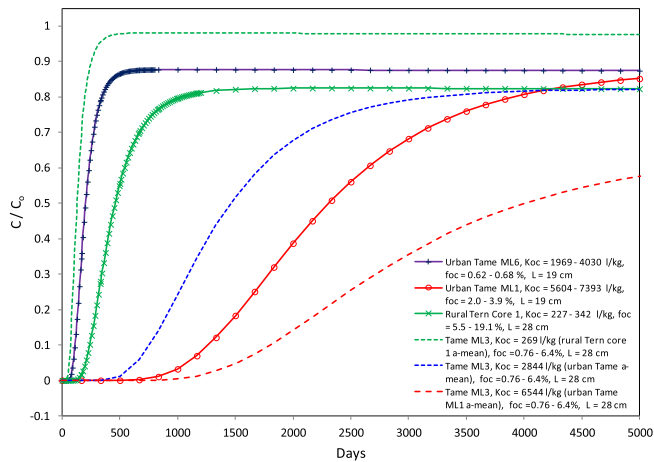
ratory  $K_d$ -based sorption parameter values. These show earliest breakthrough for the urban Tame ML6 core; this is largely a consequence of the low  $f_{oc}$  of the profile out-weighing the effects of its relatively high  $K_{oc}$ . The next breakthrough is predicted to be for the rural Tern core 1 which, in contrast with the Tame core, has a high  $f_{oc}$  and a low  $K_{oc}$ : though the breakthrough is delayed relative to the Tame ML6 core, the travel distance is around 50% longer, and the PCE velocities are similar. The Tern core contrasts with the Tame core in having a high  $f_{oc}$  but low  $K_{oc}$ .

The most retarded breakthrough of the cases using the laboratory parameter values is for the Tame ML1 core. In this case, breakthrough to  $C/C_0 = 0.5$  takes around 2300 d and to equilibrium breakthrough about 5000 d compared to around 500 d for the ML6 core. Both these profiles ultimately plateau around the same concentration which is a consequence of degradation just occurring in the dissolved-phase where they spend similar times. The significant retardation of the ML1 case is due to its very high  $K_{oc}$  and moderately high  $f_{oc}$  resulting in  $R$  values over 1000 (Fig. 6). The PCE breakthrough over this thin (19 cm) riverbed deposit occurs over a period of 2 to 14 years from the arrival of the PCE at the base of the deposit. This is much greater than the groundwater travel time of 2 days. It is quite probable that the ML1 deposits have a hydraulic conductivity up to at least an order of magnitude lower than modelled, thus making the residence times even greater. It is clear that PCE residence within even thin (<20 cm) riverbed sediments may be measured in decades, though this presumes that the sediment and solid phase OM lifetimes are also at least similarly large.

The dashed curves lacking markers in Fig. 10 are for Tame core ML3, which has a variable  $f_{oc}$  (Fig. 3). The curves presented are for a range of  $K_{oc}$  values that might be used in practice. The sensitivity to  $K_{oc}$  is seen to be significant in that the curves presented include breakthrough times both faster (rural Tern  $K_{oc} = \text{US EPA } K_{oc}$ ) and slower (Tame ML1 arithmetic mean  $K_{oc}$ ) than any of the systems so far discussed. The simulations show clearly the significant error in residence times predicted when using the US EPA (1996)  $K_{oc}$  inappropriately where TACM is a significant contributor to the  $f_{oc}$ .

### 5.3. Simulations evaluating bioavailability assumptions

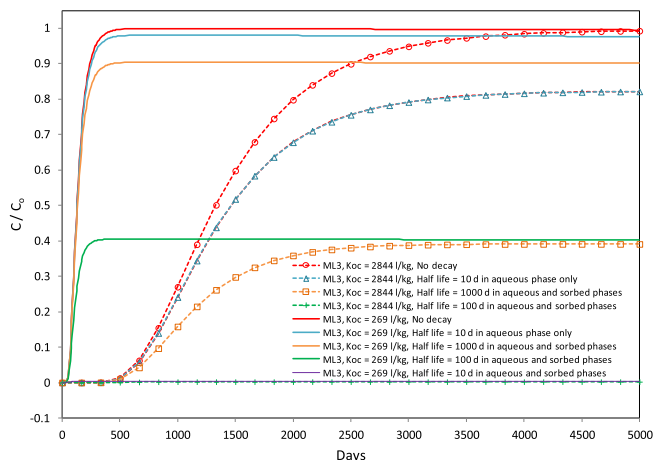
Fig. 11 illustrates the sensitivity to the bioavailability assumption using the ML3 core (length = 28 cm). Four of the curves lacking markers are for the low  $K_{oc}$  (absorption dominant) case with different decay constants: the fifth is for decay in the aqueous phase only. Breakthrough is rapid for the no-decay and aqueous-only decay cases, the latter rising nearly to input concentrations ( $C/C_0 = 1$ ) despite a half-life of only 10d. It is clear that for the system studied, decay occurring only in the aqueous phase is unlikely to affect attenuation significantly. The other 3 curves lacking markers show, however, the significant influence of allowing contaminant decay of the sorbed PCE. Even a long half-life of 1000 d causes



**Fig. 10.** Simulated breakthrough curves for Tame and Tern riverbed core adopting various  $K_{oc}$  assumptions and core  $f_{oc}$  profile data shown in Fig. 3 (all profiles assume a half life of 10 d with degradation only possible in the aqueous phase).

the equilibrium concentration to drop to  $0.9C/C_0$ ; a 100 d half-life results in an equilibrium concentration of  $0.4C/C_0$ , and no breakthrough (i.e., complete attenuation) is seen in the case of a 10 d half-life. The latter result is in complete contrast to the 10 d half-life case where decay occurs only in the aqueous-phase and equilibrium relative concentrations were close to unity ( $C/C_0 = 0.98$ ). The significance of the bioavailability assumption is hence clear.

The curves with markers in Fig. 11 are for the high  $K_{oc}$  (adsorption dominant) case and show delayed breakthrough in all cases due to the increased sorption. Rise to  $C/C_0 = 1$  for the no-decay case now requires about 4000 d (compared to 400 d for the low  $K_{oc}$  case). The 10 d half life applied to just the aqueous phase results in only modest attenuation with a  $0.8C/C_0$  plateau. The influence of allowing biodegradation of the sorbed phase causes even a very long half life of 1000 d to attenuate the breakthrough to a  $0.4C/C_0$  plateau (a 100 d half life was required to achieve this equilibrium concentration for the low  $K_{oc}$  case). A 100 d half life results in complete attenuation and no breakthrough. Hence, as expected, the significance of the bioavailability assumption is even more apparent in the more highly sorbing case. The models illustrate quantitatively that even quite a long half life may result in complete attenuation of breakthrough if a sorbed phase has bioavailability, but even very short half-lives may have very limited effects if



**Fig. 11.** Simulated breakthrough curves for Tame ML3 riverbed core that use ML3  $f_{oc}$  profile data shown in Fig. 3 (core length = 28 cm) for representative rural and urban  $K_{oc}$  estimates and a range of degradation assumptions that illustrate the significance of bioavailability assumptions.

degradation occurs only in the aqueous phase. Without resolution of this assumption, predictions could range from complete breakthrough to none at all.

## 6. Conclusions

Greater PCE sorption, and therefore increased residence time, occurred in the study's urban riverbed deposits than in the study's rural riverbed deposits. This was shown to be due to the presence of highly-sorbing sediments containing organic matter rich in TACM of anthropogenic origin. The evidence for this was obtained from PCE batch sorption experiments and OM characterisation of riverbed sediments from urban and rural sites. The implications of the findings were quantitatively investigated by modelling, which showed the contrast that may occur between urban and rural riverbed deposit residence times, and also the substantial sensitivity to bioavailability assumptions.

Sorption in the rural riverbed sediments is controlled by the presence of recent OM to which absorption partitioning may occur. This process is very well predicted using the US EPA (1996) empirical  $K_{oc,e}$  for PCE. Whilst  $K_{oc}$  values are relatively low due to the presence of 'natural' organic matter, sorption in this lowland, low-velocity rural river is relatively high due to the sediment's high  $f_{oc}$ . In contrast, the urban riverbed sediments were found to exhibit much more variable, but often significantly higher  $K_{oc}$  than the rural sediment and US EPA  $K_{oc}$  values.  $K_{oc}$  values in the urban deposits are typically around an order of magnitude or more greater than in the rural deposits, and are similar to literature  $K_{oc}$  values for TACM where sorption is attributed to adsorption rather than absorption. This presence of TACM was confirmed by organic petrography analysis that showed that the urban riverbed sediment OM was dominated by a diversity of TACM materials with a high proportion of coal, coke and coal hydrogenation residue. This material can be attributed to river transport of particles released from extensive up-catchment coal mining, coal mining related industry (e.g. coal gasification, smelting), and road discharges amongst other potential urban inputs.

It is concluded from the sorption data and modelling results that the presence of TACM in urban riverbed deposits may result in order of magnitude increases in PCE residence times. This would mean that years to a decade or more may be required for PCE to breakthrough through even thin (c. 25 cm) riverbed deposits where groundwater requires only days. Under the standard assumption that the sorbed contaminant is not bioavailable, biodegradation in the dissolved-phase occurs for such a limited proportion of time in highly-sorbing sediments that attenuation of breakthrough is insignificant unless the half-life is very low. In such highly-sorbing systems the assumptions on bioavailability become critical. If biodegradation occurs in the sorbed phase, even moderate to quite long half-lives may cause complete attenuation of a discharging contaminant plume. Overall, contaminant residence times within urban riverbed environments may be expected to vary greatly with significant sensitivity to sorption and biodegradation occurrence and bioavailability controls.

Whilst the catchment is one of the most urbanised in the UK, it is reasonably anticipated that many catchments around the world will be sufficiently urbanised that similar enhanced sorption of CAH and other organic contaminants may be occurring due to the presence of TACM. Longer histories of anthropogenic activity, perhaps dating back to the 18th century Industrial Revolution or prior, may generate greater accumulated thicknesses of TACM within a riverbed. The Anthropocene period may hence be expected to have a considerable influence upon modern-day contaminant residence time and fate within an urban riverbed. Sediments impacted by urban pollution or activities that have a

significant presence of TACM cannot be assumed to have the property values usually assigned to other Quaternary sediments. A yet further consequence of contaminant accumulation in high-sorption potential sediments is that sudden release of this stored pollutant may occur with sediment re-suspension during flood events resulting in particle-facilitated contaminant transport and possible significant influence upon river-water quality (Schwientek et al., 2013; Rügner et al. 2013, 2019).

Future research is needed: to determine how TACM amounts can be estimated in a practicable way in riverbed deposits; to delineate the spatial distribution and depth in the riverbed of the elevated TACM -high sorption layer and its dynamic movement (during flood events); and, to establish the bioavailability of contaminants sorbed to both NOM and TACM. Related system complexities also require assessment, including non-linearity of sorption with concentration, and sorptive/partitioning interactions with bacterial cell compartments and/or exopolymeric substances of varying hydrophobicity (Leitner et al., 2018; Renpenning et al., 2015). Whilst TACM is relatively recalcitrant and not expected to act as an electron donor in CAH biodegradation, it can clearly cause significant increases in contaminant residence times. It is hence necessary to establish if prolonged residence times coupled with supply of labile DOM electron donors from surface water penetration of the sediments (Freitas et al., 2015), alongside some labile NOM already present in the sediments, is sufficient to result in biodegradation of adsorbed and/or absorbed contaminants.

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